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THE PURITY OF NICKEL SALTS¹

¹Further details of this investigation have been published in an article by M. R. Thompson and C. T. Thomas - Trans. Amer. Electrochem. Soc. 42, September 1922.

I. INTRODUCTION

During recent years the Bureau of Standards has received numerous inquiries from various sources regarding the effect of impurities upon nickel deposition and the amounts of such impurities that may be allowable in commercial nickel salts. To establish a basis of discussion between producers and users, rather than to attempt to set up an arbitrary standard of quality, a number of samples of nickel salts have been analyzed. It was apparent from the results obtained that there exists a very great variation in the purity of this material. A study was also made of the effect upon the deposit of varying amounts of several of the principal impurities found to be present. Combining the two investigations, a tentative specification for the purity of nickel salts was drawn up.

It must be recognized that the attainment of a very high degree of purity might cause a prohibitive increase in cost. A fair proportion of the samples examined, however, would pass the specification and several samples of commercial material were entirely free of the most troublesome impurities. This situation ought to exclude the question of increased cost from the present discussion.

II. COMPOSITION OF COMMERCIAL NICKEL SALTS.

Table 1

Analyses of Nickel Salts

A - Nickel Sulphate (Single Salt)

Sample No.	% Zinc	% Copper	% Iron	% Free Acid
1	---	.011	---	---
2 ^x	---	.039 ^x	---	---
3 ^x	---	.005	.130 ^x	.020
4	---	---	.045	.015
5 ^x	.120 ^x	.050 ^x	.020	.210 ^x
6	.044	.014	.040	.040
7	---	.018	.100	.025
8 ^x	.088 ^x	.010	.110 ^x	.075
9 ¹	.010	.016	.100	---
10 ^x	.016	.024 ^x	.070	---
11 ^x	.010	.034 ^x	---	---
12 ^x	.010	---	.120 ^x	---
13	---	.005	---	---
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Average	.022	.017	.057	.030

¹ Samples 9-12, inclusive, were from four different barrels of the same shipment.

^x Samples marked x would be rejected by the specification proposed in Table 4.

B - Nickel Ammonium Sulphate
(Double Salt)

Sample No.	% Zinc	% Copper	% Iron	% Free Acid
14 ^x	---	.045 ^x	---	---
15 ^x	---	.058 ^x	.025	.030
16	---	---	---	---
17 ^x	.028	.050 ^x	.035	.070
18	.010	.017	.024	.070
Average	.008	.034	.017	.034

^x Samples marked x would be rejected by the specification proposed in Table 4.

The amounts of insoluble matter and of chloride were usually very small. No appreciable amount of arsenic could be detected in these samples. Magnesium sulphate may be present; one otherwise very pure lot contained over four percent. This substance has sometimes been added to the bath as a "conducting salt" and is not known to have any injurious effect, but its presence in nickel salts is undesirable from the standpoint of lowering the nickel content of the latter. Small amounts of cobalt sulphate are often found. The properties of nickel and cobalt are so nearly alike that small amounts of the latter could hardly be important. No other impurities were included in the present investigation, our conclusion being that zinc, copper and iron were the principal impurities to be considered.

III. EFFECT OF IMPURITIES UPON THE NICKEL DEPOSIT.

A number of deposits were prepared using still solutions of the following composition:

Table 2.

Composition of Nickel Baths			
	Normality	g/L	oz/gal
Nickel Sulphate (7 H ₂ O)	1.00	140	19
Ammonium chloride.....	0.35	14	2
Boric acid.....	0.25 (M)	16	2

Commercial 95-97% nickel anodes were used and the deposits were made upon brass plates at a cathode current density of 1 amp./dm² (9.3 amp./sq.ft.). The time of deposition varied from one to twenty-four hours, sometimes longer, as it was desired to collect data useful in the electro-refining of nickel and the production of heavy deposits as well as in the electroplating of very thin deposits. In discussing the results, due allowance will be made for the thickness of the deposit. The acidity of the bath was controlled by means of indicators. The baths were prepared from a lot of very pure nickel sulphate and to each bath a known amount (in the form of the sulphate) of the impurity to be studied was added. Other factors were probably not of great importance in this work and will not be discussed, as commercial conditions vary considerably and our experiments were conducted solely with the idea of collecting data that would apply to them in a general way. The results of the experiments are briefly outlined as follows:

Zinc

0.03% Zinc in Nickel Sulphate. Deposits satisfactory.

0.09% " " " " " "

No certain effect of zinc was noted in these first two experiments.

0.20% Zinc in Nickel Sulphate. Possible tendency toward bright edges and pitting, but rather good deposits on the whole.

0.30% Zinc in Nickel Sulphate. Distinct tendency toward bright edges, bright splotches on surface and pitting.

Deposit very smooth and little, if any, gassing.

0.44% Zinc in Nickel Sulphate. Strong gassing from the start of deposition. Deposits loose, black and scaly from the start.

Copper

0.005% Copper in Nickel Sulphate. Deposits satisfactory.

0.025% " " " " " "

No definite effect of copper noted in these first two experiments.

.050% Copper in Nickel Sulphate. A few small dark trees, or "burrs", near bottom edge.

.100% Copper in Nickel Sulphate. Treed all over, with dark gray spongy deposit at bottom.

.500% Copper in Nickel Sulphate. Deposits as above, but highly exaggerated.

The first noticeable effect of zinc seems to be a tendency toward bright edges and smooth, lustrous deposits. An increased amount of zinc brings out bright lines, spots and patches, also pits, although the latter may be separate from the bright spots. Excessive amounts of zinc cause gassing at the cathode, attended by a very characteristic loose, black, scaly deposit, which is apparent from the start of deposition.

The first noticeable effect of copper seems to be a tendency toward a darkening of the deposit and slight roughness near the bottom edge, caused by scattered dark trees or "burrs". Pitting is also likely to appear. A larger amount of copper causes this roughness to spread all over the cathode. Excessive amounts of copper cause, in addition, a very spongy dark grey voluminous deposit at the bottom. These effects are quite characteristic. There seems to be no especial tendency toward gassing at the cathode.

In both cases, where moderate amounts of the impurity are present, a deposit may appear normal at the start, but gradually get poor as it becomes thicker. If the concentration of the impurity is great enough, a deposit will be poor from the start of deposition.

Commercial nickel anodes contain copper, usually from 0.10 to 0.25%. It has been found, however, that most of this copper goes into the anode sludge rather than into solution. The necessity exists, therefore, of restricting the copper in the nickel salts, whether or not copper is present in the anodes.

It is believed that maximum amounts of 0.05% zinc and 0.02% copper constitute a reasonable specification for these metals at this time. Copper seems to be the more troublesome impurity of the two and therefore the limiting amount is made lower than in the case of zinc. Larger amounts than these may be present without causing poor deposits, but a fairly wide margin of safety is necessary, both on general principles and because the occasional addition of salts to the bath might produce an accumulation of an impurity at any time (especially in the case of zinc, which deposits after nickel according to the electrochemical series). The amounts suggested refer especially to thin plating deposits and it would be advisable to have even lesser amounts present when very heavy deposits are being made.

Iron. The study of iron has not yet been completed and it is planned to conduct an extended investigation, the results of which will be published later. Preliminary indications are that iron makes the nickel deposit whiter in color and finer-grained in structure, therefore presumably harder. Iron in the solution in the form of ferrous sulphate has a strong tendency to deposit and several per cent of iron will often be found present in commercial nickel deposits. More would be present if ferrous sulphate were not constantly oxidizing, resulting

in the precipitation of a basic ferric salt, which is usually the cause of the turbidity of nickel plating baths. There are indications that this precipitate may tend to cause porous nickel deposits.

Most European writers regard curling and cracking as principally due to iron and advise a periodical removal of iron from the bath. We have made a number of heavy deposits containing up to 7% of iron, without the occurrence of curling or cracking. It does not seem possible to state definitely at the present time and with the limited knowledge of the subject available, whether iron in the nickel deposit is advantageous or objectionable.

All the 95-97% anodes used in this country contain iron, usually from 0.5 to 1.5% and the 92% anodes, still used by some platers, contain 5 to 6% of iron. The plating bath, therefore always contains in solution as much iron as can remain under the operating conditions. In view of this fact, it is obviously not justifiable to attempt the complete exclusion of iron from nickel salts. The limiting amount of 0.1% that we are proposing, is equivalent to 0.5% in anodes and is believed to be a reasonable requirement until anodes can be made and used with a lower content of iron than 0.5%.

Free Acid. This is estimated as free sulphuric acid. The presence of a very large amount of free acid may be an indication of insufficient purification of the salts and it is noticeable that the sample containing the largest amount (number 5) was also badly contaminated with zinc and copper. Free acid may attack the wood or paper of containers and thereby produce soluble organic impurities that are troublesome in the bath. On the other hand, small amounts of acid are hardly deleterious in themselves, since boric acid is usually added to the bath and the hydrogen ion concentration, or degree of acidity, largely established by the boric acid, is of more importance than the total acidity. It is believed that a maximum of 0.1% free acid is a reasonable specification; this amount was exceeded only in the case of one sample (number 5).

IV. PROPOSED SPECIFICATION FOR NICKEL SALTS.

Table 3
Suggested Upper Limits of Impurities

<u>If Calculated As</u>	<u>Not Over</u>	<u>If Calculated As</u>	<u>Not Over</u>
Zinc	0.05%	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	0.22%
Copper	.02	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.08
Iron	.10	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.50
Free Acid	.10	H_2SO_4	.10
			<hr/> 0.90%
Nickel in "Single Salts" not less than 21.39% Equivalent to NiSO_4 with "6.5 H_2O "			99.10
			<hr/> 100.00%
Nickel in Double Salts not less than 14.72% Equivalent to $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$			99.10
Impurities, as above,			0.90
			<hr/> 100.00%

Since nickel sulphate contains either 6 or 7 molecules of water of crystallization, according to the conditions of manufacture, storage, etc., the nickel content has been calculated on the assumption that an equal amount of both compounds may be present, or, in effect, the salt as used will contain an average of "6.5 H_2O ".

Owing to this uncertainty in the case of the single salt and the possibility of some efflorescence or deliquescence in either case, it should be emphasized that the specification of the nickel content is no criterion of the purity of the salts and is useful only in assuring that a definite amount of nickel is obtained.

V. PURIFICATION OF CONTAMINATED NICKEL BATHS.

When a bath contains copper, it is common practice to remove this impurity by making the bath slightly acid and precipitating the copper upon scrap iron (or nickel) suspended in the bath. The same result is also secured by cleaning the anodes and allowing the copper to precipitate upon them while no current is passing. We have found that such copper upon the

surface of the anodes tends to largely redissolve when deposition is resumed (the copper contained in the material of the anodes, as previously noted, tends to enter the anode sludge). It is obvious that with this method, the anodes should be cleaned again before further deposition.

It has been known for some time that neutralizing the bath with nickel hydroxide, or carbonate, (together with agitation with air to furnish oxidizing conditions) will precipitate all the iron from the bath. We have noted during this work that such a neutralization will usually also remove the effect of any zinc or copper present. After re-adjusting the degree of acidity, it is advisable, especially in the case of zinc, to electrolyze at a high current density for a few hours to insure complete removal. Sometimes a second treatment is required. Filtration, or decantation of the solution is not absolutely necessary after the treatment, as the precipitated impurities do not tend to redissolve rapidly. Filtration is, however, desirable as an added precaution when the facilities are available.

VI. CONCLUSION

It is believed that, if the above specification is found to be consistent with the experience of those engaged in nickel deposition, there will be no serious difficulty in getting the cooperation of manufacturers in producing salts of the desired purity. In connection with the furnishing of samples of salts to be analyzed, several manufacturers have assured this Bureau of their willingness to assist in maintaining a high standard of purity for this material.



